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Greenhouse gas emissions during storage of manure and digestates: Key role of methane for prediction and mitigation

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ABSTRACT

Treatment of liquid manure and other wastes by anaerobic digestion (AD) adds to renewable energy targets, and it is thus a favorable strategy for greenhouse gas (GHG) mitigation. Both untreated manure and digestates are typically stored for a period in order to recycle nutrients for crop production, and emissions of methane (CH_4), nitrous oxide (N_2O) and ammonia (NH_3) during storage contribute to the overall GHG balance. We determined emissions of all three gases during summer and autumn storage of digestates and untreated manure in pilot-scale experiments. Using these and other data, GHG balances were calculated for treatment, post-treatment storage, and field application. The GHG mitigation potential of AD was demonstrated, but CH_4 emissions during storage dominated the overall GHG balance irrespective of treatment; hence for GHG inventories and mitigation efforts, the correct estimation of this source is critical. Current inventory guidelines from the Intergovernmental Panel on Climate Change (IPCC) estimate CH_4 emissions from manure management based on a simple classification of livestock production systems, volatile solids (VS) excreted, and annual average temperature, and the effects of treatment and management at farm level are therefore not accounted for in any detail. Two empirical models were evaluated, which instead calculate VS degradation and storage temperature with daily time steps; both models were based on concepts presented by Sommer et al. (2004). Parameters for the Arrhenius temperature relationship of CH_4 production, i.e., apparent activation energy, E_a, and pre-exponential factor, A, could be selected, for which cumulative CH_4 emissions calculated with the two models approached observed emissions. However, the magnitude of emissions during a warm period was not well reproduced, and the parameters identified for the two models differed. Sensitivity analyses showed that deviations from observations could not be explained by errors in manure storage temperature. The results thus suggest that CH_4 emissions cannot be predicted from VS and temperature alone, i.e., that the methanogenic potential changes during storage. Determination of parameters for estimation of CH_4 emissions from manure management is discussed with reference to recent literature.

1. Introduction

Animal agriculture is responsible for around 20% of non-CO_2 greenhouse gas (GHG) emissions such as nitrous oxide (N_2O), methane (CH_4) and fluorinated compounds (Owen and Silver, 2015). Globally, manure management contributes about 10% of agricultural CH_4 emissions (Yusuf et al., 2012), but in confined livestock production systems (e.g. dairies and piggeries) with liquid manure management this proportion can exceed 50% depending on climate (Owen and Silver, 2015). Furthermore, Davidson (2009) estimated that management and field application of livestock manure overall accounts for 44% of total anthropogenic N_2O emissions. These figures emphasize the need to improve estimates of GHG emissions from manure management.

Country-specific practices for manure management significantly influence GHG emissions (Sommer et al., 2009). For example, in Denmark around 80% of livestock manure is managed as slurry (Foged, 2012), most of which is stored until spring for land application as fertiliser due to regulatory provisions to enhance nitrogen use efficiency (Danish Environmental Protection Agency, 2012). Methane emissions during liquid manure storage can thus be significant due to its high

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content of degradable organic matter (volatile solids, VS) and predominantly anaerobic conditions (Umetsu et al., 2005; Sommer et al., 2007).

Several manure treatment technologies have the potential to modify CH_4 emissions (Hou et al., 2015). An increasing proportion of liquid manure is treated by anaerobic digestion (AD) in an effort to capture the CH_4 produced during VS degradation for bioenergy purposes (Nkoa, 2014; Dhamodharan et al., 2015), and this may reduce CH_4 emissions from the manure during post-treatment storage (Amon et al., 2006; Nkoa, 2014). Predicting CH_4 emissions from digestates, however, is complicated by the fact that manure is often co-digested with other wastes, and how this affects emissions during storage depends on the substrate composition (Rodhe et al., 2015), as well as process parameters (Triolo et al., 2011) and storage conditions (Clemens et al., 2006; Wood et al., 2012). The degradation of VS during AD also leads to net nitrogen (N) mineralization (Koirala et al., 2013), which increases the potential for emissions of N_2O and ammonia (NH_3), an indirect source of N_2O, during storage (Misselbrook et al., 2005; Nielsen et al., 2010). Determining the net GHG balance of contrasting treatment and management practices thus requires that emissions of N_2O and NH_3 are also quantified.

National GHG inventories for agriculture are based on guidelines proposed by the Intergovernmental Panel on Climate Change (IPCC, 2006), in which annual CH_4 emissions from manure management are estimated from bioavailable VS in excretal returns and CH_4 conversion factors for a limited number of livestock production systems, and average annual temperature. This approach assumes that a methanogenic potential is present and not a limiting factor. Annual emissions of N_2O and NH_3 are similarly estimated using emission factors (EFs) and total manure N. However, annual EFs are not suited to describe the dynamic changes resulting from treatment and variable retentions time in barns and outside storage, and therefore a prediction model with higher temporal resolution is needed.

In the present study, GHG balances were determined, and two empirical models for prediction of CH_4 emissions evaluated, using data from pilot-scale storage experiments with four different liquid manure materials as case. Two management practices involving AD were represented, as well as untreated cattle and pig slurry for reference. We hypothesized i) that AD treatment would reduce CH_4 emissions during storage compared to untreated slurries; ii) that the overall GHG balance of scenarios with AD would be lower than those of untreated manure; and iii) that CH_4 emissions during storage of liquid manure materials could be predicted from VS composition and storage temperature.

2. Model applications

Sommer et al. (2004) proposed an empirical model to estimate daily CH_4 emissions based on concentrations of total and degradable volatile solids (VS, kg) excreted, storage temperature, and duration of storage. The model distinguished two pools of VS, i.e., an easily degradable fraction (VS_d, kg kg^{-1} VS) and a "non-degradable" fraction (VS_{nd}, kg kg^{-1} VS) with a much slower decomposition rate set to 1% of the rate for VS_d:

$$F_{CH4} = (VS_d + 0.01VS_{nd})\, e^{\left[\ln(A) - \frac{E_a}{RT}\right]} \times 24 \quad (1)$$

where F_{CH4} is CH_4 emission rate (g CH_4 kg^{-1} VS day^{-1}), A is the pre-exponential factor (g CH_4 kg^{-1} VS h^{-1}) and E_a the apparent activation energy (J mol^{-1}) of an Arrhenius equation describing the temperature response of CH_4 production, R the gas constant (8.314 J mol^{-1} K^{-1}), and T is temperature (K). Two modified versions of this model were applied here to evaluate the feasibility of this approach against observations, though only for cattle slurry (treatment *CS*, cf. Section 3), since parameters for both models were not available with the other materials.

2.1. Integrated farm system model (IFSM)

The sub-model of the Integrated Farm Systems Model (IFSM) for CH_4 emissions from manure management in beef and dairy production systems (Chianese et al., 2008; USDA-ARS, 2009) shares several features with the model of Sommer et al. (2004). The IFSM has been used in several studies to assess the impact of GHG reduction strategies for dairy and beef farms (e.g., Rotz and Hafner, 2011; Dutreuil et al., 2014). The model performance in predicting CH_4 emissions during manure storage has not been extensively verified, but Chianese et al. (2009) did predict annual CH_4 emissions using 25 years of weather data and found that the results were in good agreement with an on-farm monitoring study (Husted, 1994), in which observed daily CH_4 emissions from a cattle slurry storage tank varied between 5 and 35 g CH_4 m^{-3} d^{-1} during a 12-month monitoring period.

The IFSM model adopts Eq. (1) to calculate CH_4 emissions and uses the Arrhenius parameters proposed by Sommer et al. (2004), i.e., an E_a value of 112.7 and ln(A) value of 43.33. A modification to the original model has been introduced to calculate the fraction of degradable VS (VS_d) as a function of the VS contained in the manure storage on a given day using Eq. (2):

$$VS_d = \left(VS_{in}.\left(\frac{B_0}{E_{CH4,pot}}\right) - VS_{loss}\right)/VS_T \quad (2)$$

where VS_T is the total volatile solids contained in the storage tank on a given day (kg), VS_d the degradable VS fraction in the manure (kg kg VS^{-1}), VS_{in} the VS loaded into the storage tank up to the given day (kg), B_0 the achievable emission of CH_4 during anaerobic digestion (0.2 kg CH_4 kg^{-1} VS, cf. Sommer et al., 2004), $E_{CH4,\ pot}$ the potential CH_4 yield of the manure (0.48 kg CH_4 kg^{-1} VS, cf. Sommer et al., 2004), VS_{loss} the VS lost from the storage up to the given day (kg), which is predicted in IFSM as three times the CH_4 loss from the stored manure. Secondly, VS_T is calculated as a function of the total solids (TS) content in the manure (Eq. (3)):

$$VS_T = M_{manure}.\, P_{TS}.\, P_{VS} - VS_{loss} \quad (3)$$

where M_{manure} is the accumulated mass of manure entering the storage tank (kg), P_{TS} the total solids (TS) content in the manure (kg TS kg^{-1} manure), and P_{VS} the fraction of VS in TS (0.726 kg VS kg^{-1} TS, cf. Chianese et al., 2008).

Storage temperature is an important driver of CH_4 emissions from liquid manure in both models. The IFSM model uses a 10-day moving average of daily air temperature (Chianese et al., 2009), and this approach was maintained here.

2.2. Modified Sommer model

An alternative adaptation of the model of Sommer et al. (2004) was recently proposed (Petersen et al., 2016a), which introduced new parameters for the Arrhenius temperature response function. An E_a value of 81 kJ mol^{-1} determined by Elsgaard et al. (2016) was used, and a ln(A) value of 31.2 g CH_4 kg VS^{-1} h^{-1} which was derived from CH_4 production rates in slurry collected from several cattle barns (Petersen et al., 2016a).

In the original model, VS_d was estimated from the composition of fresh excreta, but VS degradation would have already taken place during pre-storage prior to the pilot-scale experiment, and therefore the model was modified to determine VS_d experimentally (cf. section 3.2). It was further assumed that CH_4 and CO_2 were the only significant carbon (C) compounds produced during VS degradation (Spellman and Whiting, 2007), and the CH_4-C/(CH_4-C + CO_2-C) ratio observed in treatment *CS*, i.e., 0.55, was therefore used to calculate daily VS loss. This was done using Eq. (1), since daily CH_4-C emission could then be converted to daily total C loss by dividing with 0.55; C loss in turn was converted to VS loss assuming a C content in VS of 0.43 kg kg^{-1}

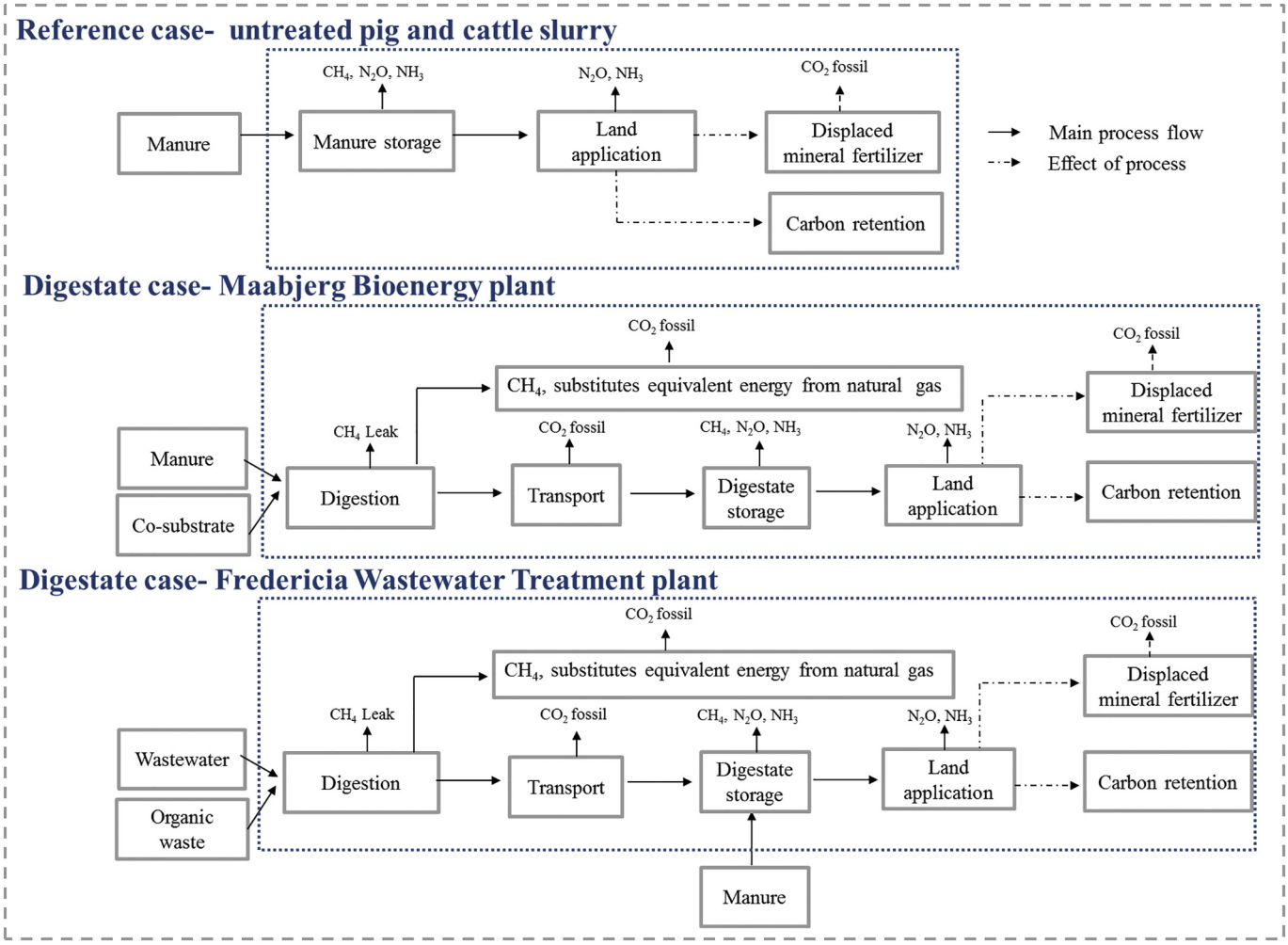

Fig. 1. System boundaries and process flow for the anaerobic digestates and untreated manure. Solid and dashed lines represent the main process flow and effects of processes, respectively.

(Petersen et al., 2016a). Residual VS_d and VS_{nd} were calculated with daily time steps.

Temperature sensors were installed in order to record slurry temperature for use in the model, but unfortunately, due to a technical problem, these data were lost, and instead manure temperature was estimated from air temperature, as in IFSM, but using a 5-day moving average to acknowledge the existence of temperature gradients near the surface of stored slurry, and the smaller scale of this storage experiment compared to on-farm storage (Rodhe et al., 2009).

3. Experiments

The study included two pilot-scale manure storage experiments, the first ('Summer') of which ran from June 2014 to April 2015 (with continuous monitoring during 90 d, and subsequently one week per month), and the second ('Autumn') from October to December 2015 (with 78 d of continuous monitoring). A detailed account of the storage experiments and monitoring results is available as online Supplementary Information, and here only a brief description of the experimental part is included.

3.1. Manure materials

Untreated pig slurry from sows and finishing pigs, and cattle slurry mainly from dairy cattle, were obtained from storage facilities at the agricultural research centre of Aarhus University. For the Summer experiment, the untreated slurries were obtained from fully mixed storage tanks where the slurries had been stored for *c.* 3 months prior to the pilot-scale experiment. For the Autumn experiment, untreated slurries were obtained from pre-tanks outside animal confinements, i.e., the age of slurries was < 1 month. Digestate was supplied by Maabjerg Bioenergy A/S in Holstebro (56°24′ N, 8° 37′ E), a centralised biogas plant processing approx. 550,000 Mg manure per year, mainly from cattle, pigs and mink, together with ca. 120,000 Mg of other organic residues, mostly from dairy industries and energy crops. The plant has six anaerobic digesters operating at mesophilic temperature (37 °C) with a hydraulic retention time (HRT) of 23 days. Also, digested and dewatered sludge was obtained from Fredericia Wastewater and Energy A/S (FWE) in Fredericia (55°33′ N, 9° 43′ E). The FWE plant processes wastewater from the municipality of Fredericia, and organic waste from local industries. The plant has two reactors operating at 40 °C, and HRT is 35 d. Traditional handling of digested and dewatered sludge involves storage until field application, but due to self-heating the potential for loss of N is high (Hansen et al., 2006), and FWE instead delivers the sludge to local farms, where it is mixed with livestock slurry in storage tanks, preserving plant available N. For the storage experiment, digested and dewatered sludge was stored together with cattle slurry.

3.2. Storage experiments

Approximately 4 Mg of each material were stored in duplicate at the pilot-scale storage facility described by Petersen et al. (2009). The

treatments were i) Maabjerg Bioenergy digestate (treatment *MBD*); ii) untreated pig slurry (treatment *PS*); iii) untreated cattle slurry (treatment *CS*), and iv) a mixture of untreated cattle slurry and digested and dewatered sewage sludge (treatment *CS + DDS*; 1:2 *w*/w based on VS). Subsamples of all materials were collected during filling for analysis of TS, total and degradable VS, total and ammoniacal N, total organic carbon, phosphorus, potassium, pH and electrical conductivity. Specifically, degradable VS (VS_d, kg kg^{-1}) was determined as described by Baral et al. (2016) from the ratio between CO_2-C released during aerobic incubation and total organic C (TOC) as:

$$VS_d = \frac{\Delta CO_2 - C}{TOC}, \quad (4)$$

where $\Delta CO_2 - C$ represents net release of CO_2-C during a 14-day aerobic incubation.

Methane, CO_2 and N_2O emissions during storage were determined in air collected from the continuously ventilated storage tanks; ventilation air was sampled at 15 min intervals in alufoil gas sampling bags, which were replaced weekly. Ammonia emissions were determined by collection of NH_3 in acid traps that were included in all gas sampling lines. Manure materials from the first storage experiment were subsequently used for a field plot experiment (Baral et al., 2017).

3.3. Greenhouse gas balances

Experimental data were used to calculate GHG balances for manure management and field application; GHG emissions from the barn were not included. A schematic overview of the scenarios analysed is presented in Fig. 1. In the GHG balances, emissions associated with storage (this study) and field application (Baral et al., 2017) were based on experimental results. Field application of 100 kg NH_4^+-N ha^{-1} was used as the baseline for all manure materials, a scenario investigated in the field plot experiment (Baral et al., 2017). One-hundred year global warming potentials (GWP_{100}) for CH_4 and N_2O of, respectively, 34 and 298 (Myhre et al., 2013) were assumed.

Methane production during AD was calculated (cf. Mikkelsen et al., 2013) as:

$$P_{CH4} = \varepsilon\ VS\ B_0\ 0.67, \quad (5)$$

where P_{CH4} is the CH_4 production (kg), *VS* is the input of volatile solids to a digester (kg); B_0 is the maximum CH_4 production capacity which was set to 0.30 and 0.35 m^3 kg^{-1} VS for the sewage sludge in treatment *CS + DDS* and the Maabjerg digestate in treatment *MBD*, respectively (IEA Bioenergy, 2014); ε is a conversion efficiency factor set to 0.9 to account for the fact that actual CH_4 yields are typically lower than B_0, and 0.67 converts from volume (m^3) to mass (kg) of CH_4. A 33% loss of carbon in VS during digestion was assumed (Möller, 2009). Methane produced during AD was converted to energy assuming 53.43 MJ kg^{-1} CH_4 (Pugesgaard et al., 2014), and was assumed to replace the equivalent amount of natural gas at 47.1 MJ kg^{-1} (USDE, 2011). Digester leakage was assumed to be 3% of CH_4 produced (Ebner et al., 2015). Emissions of CO_2 during one-way transportation (2.7 kg CO_2 L^{-1} diesel) of digestates were calculated assuming a fuel consumption of 0.0265 L diesel Mg^{-1} km^{-1} (Boldrin et al., 2016).

Ammonia emissions during storage were included as an indirect source of N_2O according to IPCC (2006). Emissions of NH_3 after field application were considered to be negligible, since application was by direct injection (Sommer and Hutchings, 2001; Hou et al., 2015). Nitrous oxide emissions from fuel combustion during farm operations were also not considered. The fraction of N lost via leaching was considered to be 28% of total N applied, and with an N_2O emission factor of 0.0075 (Nielsen et al., 2017). For untreated manure the retention of C in soil was taken to be 22% of field-applied C as estimated by Taghizadeh-Toosi and Olesen (2016) for a 20-year time horizon. For digestates, C retention was set to 35% by scaling results from Thomsen et al. (2013) to a 20-year period. The amount of mineral fertiliser N substituted by manure materials was reported by Baral et al. (2017), and was accounted for in the GHG balance by assuming a reduction of 5.6 kg CO_2 kg^{-1} fertiliser N substituted (Yara, 2016).

3.4. Data analyses

3.4.1. Cumulative GHG emissions

Cumulative GHG emissions (kg CO_{2e} m^{-3}) during Summer and Autumn storage experiments with four manure materials were analysed separately; results were log transformed to meet model assumptions about normal distribution and variance homogeneity. Cumulative emissions of CH_4, N_2O, and NH_3 were tested using the model:

$$y_{ij} = \mu + \alpha_i + \alpha\beta_{ij} + \varepsilon_{ij} \quad (6)$$

where y_{ij} is the flux of CH_4, N_2O, or NH_3 for slurry type *i* and block *j*; μ is the general mean response; α_i is the effect of slurry type *i*; $\alpha\beta_{ij}$ is the random effect of block *j* in slurry type *i*; and ε_{ij} is the residual error term. Pairwise comparisons were made by *lsmeans* using the adjusted Tukey method. The data were analysed using the '*lme*' function of the '*nlme*' package after fitting the data in Eq. (6) using R-software version 3.1.1 (R Core Team, 2014).

3.4.2. Sensitivity analyses

Several studies have shown that manure temperature can exceed the air temperature in late summer, autumn and winter (e.g., Rodhe et al., 2009; Baldé et al., 2016). Rodhe et al. (2009) found, under climatic conditions close to those of our experiment, the slurry temperature to be 1 to 3 °C higher than air temperature between August and October, and this difference can be even greater in winter. Since in the models for CH_4 emissions, slurry temperature was derived from air temperature, a sensitivity analysis was carried out to assess effects of any error in storage temperature on predicted CH_4 emissions. Simulations changing manure temperature by +1, +2 and + 3°C starting 1 August were performed with both models.

The temperature sensitivity of CH_4 emissions from manure further depends on the parameterisation of the Arrhenius relationship (cf. Eq. (1)). Model performances were evaluated with three sets of parameters: i.e., the default parameter values used in IFSM (Rotz et al., 2016) and the modified Sommer model (Petersen et al., 2016a); ii. optimized values of ln(*A*) and E_a within ranges constrained by the 95% confidence limits reported by Elsgaard et al. (2016) for cattle slurry; and iii. values of ln(*A*) and E_a based on an optimization without parameter constraints. These optimisations were performed by minimising the difference between observed and simulated CH_4 emissions using the baseline storage temperatures.

4. Results and discussion

4.1. Cumulative emissions during storage

A detailed account of manure and digestate characteristics (Table S1), and temporal dynamics of CH_4, N_2O and NH_3 emissions during storage (Fig. S2), are included as Supplementary Information, and here only cumulative emissions are presented.

Cumulative emissions of CH_4 during the Summer storage period (0–90 d) ranged from 0.5 to 3.6 kg C m^{-3} (0.3 to 3.1 kg C m^{-3} during 0–90 d), and during the Autumn experiment from 0.01 to 0.2 kg C m^{-3} (Table 1). The emissions from treatment *PS* during Summer storage were low despite comparable levels of VS_d in the different treatments. One contributing factor was the fact that the CH_4-C/(CH_4-C + CO_2-C) ratio at 0.1–0.2 was lower than those of the other treatments (0.3 to 0.55), probably as a result of more convective mixing, and hence aerobic degradation of VS at the slurry-air interface, with the dilute pig slurry. When expressed relative to VS entering the storage tanks in June 2014, the cumulative emissions of CH_4 were (*PS*) 39, (*CS*) 87, (*MBD*)

Table 1
Cumulative emissions of CH_4, N_2O, NH_3, and CO_2e during the extended Summer storage period until April 2015 of 309 d, and the Autumn storage period of 78 d.

	CH_4		N_2O		NH_3		Total GHG	
	kg C m^{-3}		g N m^{-2}		g N m^{-2}		kg CO_{2e} m^{-3}	
	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn
PS	0.5c	0.1b	0.9c	12.0a	796a	13d	26b	8a
MBD	1.2b	< 0.1c	6.1b	−0.2c	667a	256a	59b	1b
CS	3.0a	0.1b	13.9a	−0.1c	93b	38c	143a	4b
CS + DDS	3.6a	0.2a	11.8a	0.8b	521a	57b	172a	11a

Values followed by different letters indicate significant differences ($p < 0.05$). Please refer to the text for abbreviations.

Table 2
GHG balances of anaerobic digestates and untreated manure materials based on field application rate of 100 kg NH_4^+-N ha^{-1}.

		MBD	CS	PS	CS + DDS
kg CO_{2e}					
1	Natural gas substitution	−921	0	0	−1761
2	Fugitive CH_4 emission during AD	305	0	0	584
3	Transportation	190	0	0	138
4	Storage emissions				
	CH_4	1910	7594	1469	8561
	N_2O	85	304	23	214
	NH_3	95	25	192	107
5	Mineral fertiliser replacement	−336	−207	−263	−235
6	Field emissions	74	329	113	927
7	Carbon retention	−585	−878	−392	−1725
8	N leaching	104	120	95	298
	GHG balance	921	7287	1237	7108

MBD, Digested slurry from Maabjerg Bioenergy plant; CS + DDS, mixture of cattle slurry and digested and dewatered sewage sludge from Fredericia waste water treatment plant based on 1:2 (*w*/w)VS ratio; CS, cattle slurry and PS, pig slurry.
The positive values represent emissions and the negative values represent reduction in emissions

54, and (*CS + DDS*) 66 g CH_4 kg^{-1} VS. These emission levels may have been higher than would be observed in practice, where storages are only gradually filled during the year and part of the VS in manure and digestates thus enters the storage during autumn and winter where storage temperatures are low. For example, Kariyapperuma et al. (2017) observed CH_4 emissions from a cattle slurry storage tank declining from 44 to 5 g CH4 kg^{-1} VS between September and January under Eastern Canadian conditions.

Cumulative NH_3 emissions corresponded to 0.4 to 3.1 g NH_3 m^{-2} d^{-1} in the Summer storage experiment (recalculated from Table 1), and were comparable to previous slurry storage experiments with untreated and digested cattle slurry (Clemens et al., 2006) and pig slurry (Petersen et al., 2013). Ammonia-N loss in the Summer experiment ranged from 3% (treatment *CS*) to 17% (treatment *PS*) of total N. In the Autumn experiment, NH_3-N loss ranged from 0.3% (treatment *PS*) to 4% (treatment *MBD*). Treatment differences reflected crust formation (data not shown) which is known to act as a barrier against NH_3 emissions (Misselbrook et al., 2005; Wang et al., 2016).

Losses of total N as N_2O in the Summer experiment ranged from 0.02 to 0.40% of total N during summer storage, and from 0 to 0.28% in the Autumn experiment. These ranges agree with other studies of N_2O emissions from manure and digestates (Rodhe et al., 2009; Petersen et al., 2013; Wang et al., 2016).

It should be acknowledged that the sampling strategy employed, i.e., quasi-continuous subsampling from ventilation air of covered storages, ensured high precision measurements, but presumably at the expense of accuracy for N_2O and NH_3 emissions, since rainwater was intercepted by the permanent cover on storage tanks. This may have influenced NH_3 emissions from liquid-air interfaces (Montes et al., 2009), as well as N_2O emissions which have been linked with the water balance of surface crusts (Sommer et al., 2000; Petersen et al., 2012). In contrast, CH_4 production in the bulk liquid phase was probably unaffected by the sampling strategy, and emission estimates were probably accurate. Surface crusts can develop a potential for microbial CH_4 oxidation (e.g., Ambus and Petersen, 2005; Nielsen et al., 2013), but there is at present little evidence that the process represents an important sink for CH_4 in open or passively ventilated storages.

4.2. Greenhouse gas balances

Storage is normally an integrated part of manure management in confined animal production systems; other phases include collection during housing, any pre-storage treatment, and field application (Gerber et al., 2013). Methane, CO_2, N_2O and NH_3 may be emitted throughout this manure management chain, and it is critical that GHG mitigation efforts consider the relative importance of GHG sources, as well as any interactive effects.

Greenhouse gas balances were calculated for the two AD and two manure reference treatments of the Summer storage experiment where stored materials were later used as fertiliser for spring barley (Baral et al., 2017). Given the mixed origin of the digestates, the AD treatment stage was taken as upstream boundary, i.e., bioenergy production was included. Downstream emissions of N_2O were associated with field application and leaching, as well as soil C retention and mineral N fertiliser replacement value. The system boundaries and process flows for reference manures and co-digestates are shown in Fig. 1.

The application rate of 100 kg ha^{-1} NH_4^+-N to spring barley in all treatments represented different amounts of total N and VS among the four manure materials mentioned above. When the GHG emission sources were expressed as CO_2 equivalents (CO_{2e}; Table 2), 76 to 95% could be attributed to storage, of which 84 to 92% were due to CH_4 emissions, consistent with other studies (Clemens et al., 2006; Rodhe et al., 2015; Viguria et al., 2015). Energy production from anaerobic digestion in treatment *MBD* compensated for 32% of GHG emissions, and thus digestate from Maabjerg Bioenergy was able to reduce the global warming potential of this manure material by 65% through a combination of natural gas and mineral N fertiliser substitution, and retention of soil C. The corresponding figure for the AD scenario represented by treatment *CS + DDS* was 32%. These scenarios, as well as the N use efficiencies and yield-scaled N_2O emissions discussed by Baral et al. (2017), show that the manure-based digestate performed better than the untreated slurries in terms of supplying plant available N while maintaining low environmental impact. The mixing of digested and dewatered sewage sludge with untreated manure, as represented by treatment *CS + DDS*, had only a marginal GHG mitigation potential. This was mainly due to the large input of organic N with a potential for environmental losses, and this strategy cannot be recommended for GHG mitigation at this time.

Post-harvest emissions associated with crop residues were not included in the GHG balances. Several monitoring studies on sandy loam soils have found N_2O emissions during autumn and winter to be low

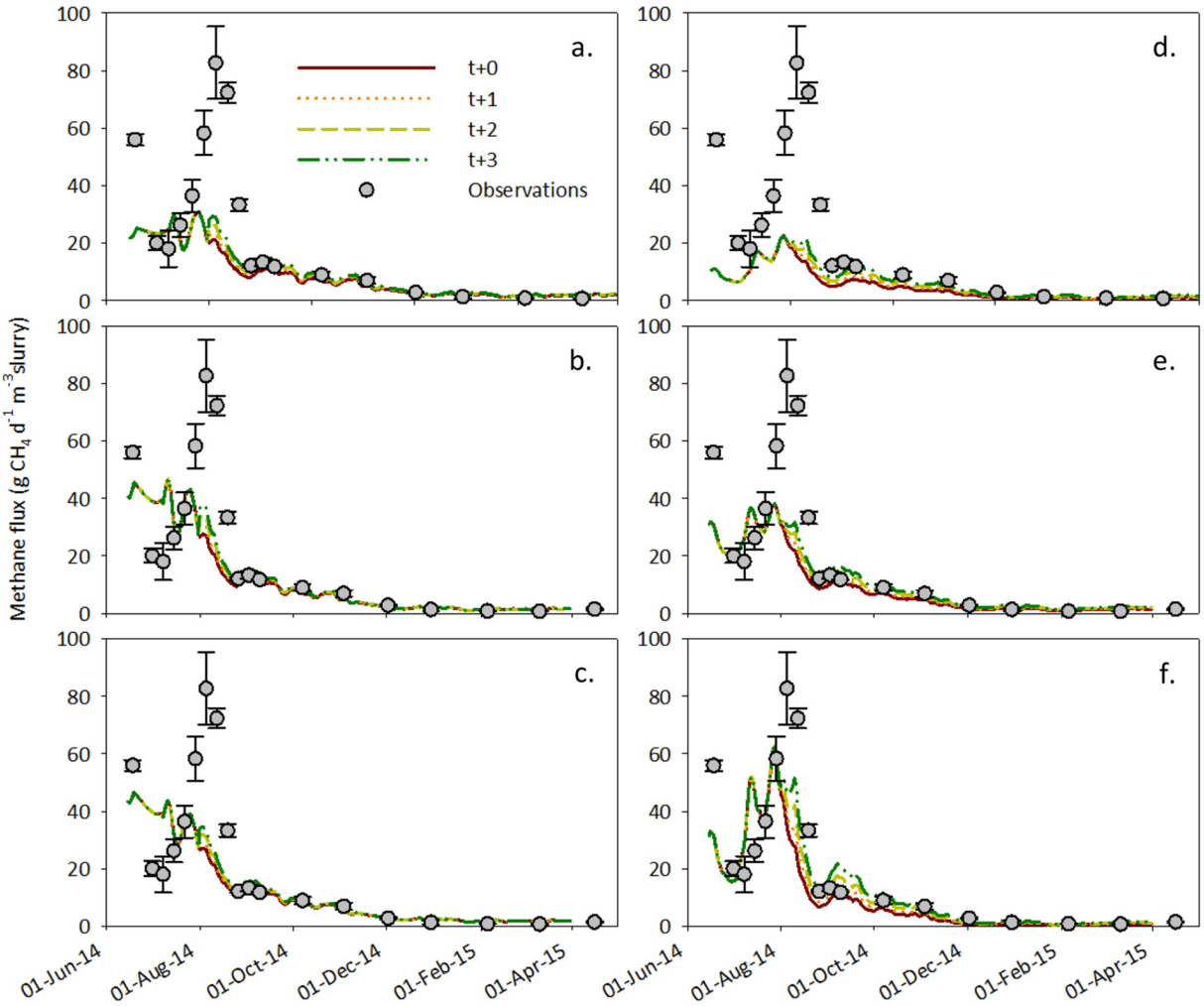

Fig. 2. Temperature sensitivity of two empirical models to simulate CH_4 emissions from cattle slurry was evaluated by changing the storage temperature from 1 August and onwards by +1 to +3 °C. The two models were the model of Sommer et al. (2004) as parameterised by Petersen et al. (2016a) (**a-c**) and the Integrated Farm Systems Model (IFSM) (**d-f**). The sensitivity test was performed using default settings for the Arrhenius parameters $ln(A)$ (g CH_4 kg^{-1} VS h^{-1}) and E_a (kJ mol^{-1}). **a**) $ln(A)$ = 31.2 and E_a = 81; **d**) $ln(A)$ = 43.33 and E_a = 112.7; **b**) and **e**) by optimisation of E_a and ln(A) within the 95% confidence limits of the parameter values determined by Elsgaard et al. (2016), i.e., 28.0 < $ln(A)$ < 32.2 and 78.2 < E_a < 88.4; **c**) and **f**) by optimisation without parameter constraints.

(e.g., Hellebrand et al., 2008; Chirinda et al., 2010; Brozyna et al., 2013), and the conclusion that CH_4 emissions during manure storage dominate the GHG balance of manure management and subsequent use therefore appears robust.

4.3. Predicting CH_4 emissions during storage

If methanogenesis during manure storage is the single largest source of GHG emissions associated with manure management and field application, then correct prediction of CH_4 emissions from storages, and effects of CH_4 mitigation measures, will be critically important. We investigated CH_4 emissions from cattle slurry in the Summer storage experiment using two empirical models, which differed in temperature response parameters, and in the modelling of manure VS decomposition.

With the modified Sommer model, CH_4 emissions from treatment *CS* (Fig. 2a) during the first week were underestimated, likely due to the release of trapped CH_4 following manure transfer to the storage tank (Sommer et al., 2000). After the first week, CH_4 emission rates were well described by the model until late July, when a rapid increase in CH_4 emissions peaking around 1 August was not captured by the model. This transient increase ended around 1 September; after this time there was again a close agreement between observed and predicted CH_4 emission rates until the end of storage in April of the following year.

The IFSM considers VS composition of fresh cattle excreta based on literature data, and the simulation was therefore started on 1 February 2014 when cattle slurry was exported from the barn. However, the CH_4 emissions predicted for the monitoring period (Fig. 2d) were very similar to those of the modified Sommer model, which means that IFSM with default parameters also failed to capture the magnitude of the increase in CH_4 emission rates peaking around 1 August. From the end of August and onwards, model predictions were slightly lower than observed emissions, and deviated more from observations than the modified Sommer model; possible reasons for this difference are discussed below.

4.3.1. Effect of storage temperature

Methanogenesis in manure is exponentially related to temperature under ambient storage conditions (Elsgaard et al., 2016). As mentioned above, manure storage temperature was in this study derived from air temperature. This approach may be valid during spring and early summer where manure volumes are typically small, whereas the difference between air and slurry temperature can be significant during autumn where cooling of the slurry is lagging behind declining air temperatures (Rodhe et al., 2009; Baldé et al., 2016). This potential error was tested by running the models assuming that slurry

temperature was +1, +2 or + 3°C above air temperature starting 1 August.

With the modified Sommer model and default Arrhenius parameters, only minor increases in predicted CH_4 emission rates were seen with increasing temperature (Fig. 2a), and furthermore no improvement in predicting the high rates during August was achieved. The cumulative CH_4 emissions did increase by up to 14%. The IFSM model (Fig. 2d) was more sensitive to manure temperature, and an increase in cumulative emissions of up to 33% was seen in the test of temperature sensitivity. These effects of storage temperature are not trivial and stress the importance of documenting temperature conditions in storages. However, the inability of both models to describe the high CH_4 emissions in August suggested that storage temperature was not the main source of model deviations, and the temperature response was therefore further explored by varying the Arrhenius parameters.

In a first sensitivity test, E_a and ln(A) were allowed to vary within the 95% confidence limits reported by Elsgaard et al. (2016). With the modified Sommer model (Fig. 2b) this resulted in higher emission estimates during August, and a better fit during autumn, but peak emissions were still not well described, and predictions for the early phase of storage (disregarding the first week) were much poorer in this case. A second re-parameterisation, in which there were no constraints on parameter estimates, did not significantly improve the fit of this model (Fig. 2c). Parameter optimisation (with or without constraints) resulted in cumulative emissions between 69 and 76 g CH_4 kg^{-1} VS, which was close to the observed emission of 87 g CH_4 kg^{-1} VS (Fig. 3a).

The optimisation of parameters ln(A) and E_a within the 95% confidence limits reported by Elsgaard et al. (2016) improved IFSM predictions, although peak emissions where still significantly underestimated (Fig. 2e). When the optimisation was repeated without parameter constraints, the peak emissions were better simulated, with maximum predicted rate of 62 g CH_4 m^{-3} d^{-1} (Fig. 2f). With default parameterization, cumulative losses of CH_4 predicted by IFSM were 40–54 g CH_4 kg^{-1} VS, or about half the observed emission. Cumulative CH_4 emissions where better predicted following the optimisation of parameters, and closer to observed emissions (Fig. 3b).

The results of sensitivity analyses are summarised in Table 3. For both models the default parameterisation resulted in poor model efficiencies (EF) of −0.1 to 0.3. The modified Sommer model was only marginally improved by permitting flexibility in parameters, whereas IFSM was more dynamic in reproducing observed CH_4 emissions, especially when combined with temperature manipulation. But even though both models could be re-parameterised to better reflect temporal dynamics and cumulative emissions, it is necessary to critically evaluate the biological relevance of model parameters.

4.3.2. Selection of Arrhenius parameters

The modified Sommer model used an apparent activation energy value derived from CH_4 production in individual manure materials (Elsgaard et al., 2016). In contrast, the E_a used in the original model (Sommer et al., 2004), and thus in IFSM, was derived from emissions of CH_4 in long-term storage experiments. The resulting E_a of 112.7 kJ mol^{-1} was considerably higher than the 81 kJ mol^{-1} of Elsgaard et al. (2016). And both values are higher than the E_a value of 63 kJ mol^{-1} currently used in the USEPA method to calculate CH_4 emissions from liquid manure storage (Mangino et al., 2001), and in the IPCC methodology (IPCC, 2006) which defines annual CH_4 conversion factors from Mangino et al. (2001). The value of 63 kJ mol^{-1} was derived from a compilation of data from AD experiments together covering a temperature range from 15 to 60°C (first presentation in peer-reviewed literature by Ashare et al., 1979). Activation energy is inversely related to substrate degradability (Li et al., 2015), and hence the values of 112.7 kJ mol^{-1} (storage in cool temperate climates of Denmark and New Zealand), and 63 kJ mol^{-1} (AD across wide range of temperatures including thermophilic conditions) could therefore be biased towards lower and higher degradability, respectively.

Trousdell et al. (2016) recently examined atmospheric CH_4 emissions over an area where sources are dominated by dairy production, and they derived an E_a of 76 kJ mol^{-1} for a temperature range of 25–36°C. Furthermore, Yvon-Durocher et al. (2014) conducted a global meta-analysis of CH_4 emissions from contrasting ecosystems for which an average E_a of 89 kJ mol^{-1} could be derived. Although activation energy of a given reaction is constant, the temperature sensitivity of microorganisms and enzymes may vary (Lloyd and Taylor, 1994), and hence the apparent E_a of CH_4 emissions from liquid manure storage could depend on climate zone. Nevertheless, the estimate of 81 kJ mol^{-1} (with 95% confidence interval [C.I.] 74.9–87.1 kJ mol^{-1}) was based on incubations at 20 different temperatures between 5 and 35°C (Elsgaard et al., 2016), and it could therefore be robust across climate zones.

In graphical presentations of Arrhenius temperature relationships, ln(A) is the intercept with the y axis, and it thus represents a CH_4 production potential as defined by substrate availability and methanogenic potential. Petersen et al. (2016a) reported an average value of 31.2 g CH_4 kg^{-1} VS h^{-1} (95% C.I. 30.7–31.8 g CH_4 kg^{-1} VS h^{-1}) for dairy cattle manure collected in barns, and Elsgaard et al. (2016) a value equivalent to 30.1 g CH_4 kg^{-1} VS h^{-1} (95% C.I. 28.0–32.2 g CH_4 kg^{-1} VS h^{-1}) for a mixture of 0–6 months old cattle slurry. Assuming a retention time in barns of 30–40 d (Kai et al., 2015), this difference in ln (A) could be explained by substrate depletion during storage. The ln(A) value used in IFSM, 43.33 g CH_4 kg^{-1} VS h^{-1}, was much higher than the two former values. Based on the information available we cannot rule out the possibility that methanogenesis in the cattle slurries were initially inhibited by an adverse chemical environment (Chen et al., 2008), and later overcame the inhibition by selective growth of methanogens adapted to the specific environment (Zeeman et al., 1985; Massé et al., 2008; Fotidis et al., 2013). On the other hand, a value of 43.33 g CH_4 kg^{-1} VS h^{-1} does seem out of range and should be further investigated.

4.3.3. Methanogenic potential

Both models assumed that Arrhenius parameters were constant during the entire storage period, but this may depend on substrate availability, as discussed by Petersen et al. (2013), and by changes in the composition and activity of methanogenic communities (Barret et al., 2013; Habtewold et al., 2018). If ln(A) increased during

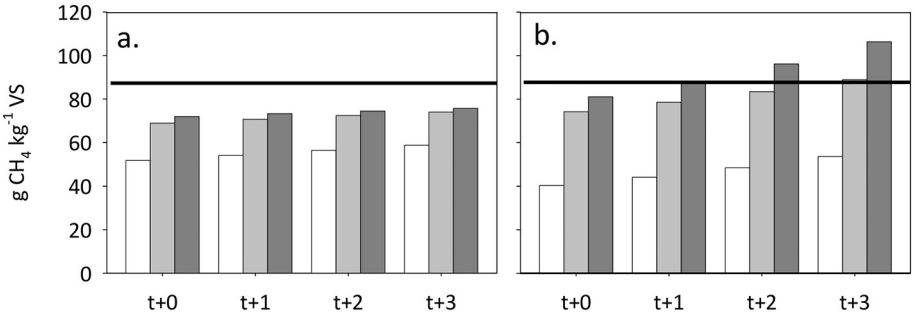

Fig. 3. Cumulative emissions of CH_4 (g kg^{-1} VS) from cattle slurry between June 2014 and April 2015 (309 d) were modelled with two empirical models: **a**) a modified version of the model of Sommer et al. (2004) and **b**) IFSM. Cumulative CH_4 emissions were calculated using default parameter values for E_a and $ln(A)$ (white bars), parameters constrained by the 95% confidence limits of parameters determined by Elsgaard et al. (2016) (light grey bars), and optimisation without parameter constraints (dark grey bars). Please see legend of Fig. 2 for additional details. The black line represents observed cumulative CH_4 emissions.

Table 3
Model performance was determined for all cases in the temperature sensitivity analysis presented in Fig. 2, which differed in parameters *ln(A)* (g CH_4 kg^{-1} VS h^{-1}) and E_a (kJ mol^{-1}). Two models were compared, i.e., the model of Sommer et al. (2004) as parameterised by Petersen et al. (2016a), and the Integrated Farm Systems Model (IFSM). Mean error (ME), relative ME, root mean squared error (RMSE), relative RMSE, and model efficiency (EF) were calculated with default parameters, with parameters constrained within 95% confidence limits of the parameters determined by Elsgaard et al. (2016), and without parameter constraints.

Sommer et al. (2004), modified

Parameters	Default				Constrained, Elsgaard et al. (2016)				No constraints			
	ln(*A*) = 31.2		E_a = 81.0		ln(*A*) = 30.7		E_a = 78.2		ln(*A*) = 22.9		E_a = 59.4	
	t + 0	t + 1	t + 2	t + 3	t + 0	t + 1	t + 2	t + 3	t + 0	t + 1	t + 2	t + 3
ME	12.4	11.9	11.4	10.8	7.0	6.5	6.0	5.5	6.6	6.2	5.8	5.5
ME (%)	48.5	46.5	44.4	42.1	27.3	25.4	23.5	21.5	25.8	24.3	22.8	21.2
RMSE	23.5	22.8	22.1	21.4	21.0	20.3	19.5	18.7	21.0	20.4	19.8	19.2
RMSE (%)	91.5	89.0	86.3	83.4	81.9	79.0	75.9	72.7	81.7	79.5	77.2	74.8
EF	0.1	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.3	0.3	0.4	0.4

IFSM

Parameters	Default				Constrained, Elsgaard et al. (2016)				No constraints			
	ln(*A*) = 43.3		E_a = 112.7		ln(*A*) = 32.22		E_a = 82.1		ln(*A*) = 58.5		E_a = 146.0	
	t + 0	t + 1	t + 2	t + 3	t + 0	t + 1	t + 2	t + 3	t + 0	t + 1	t + 2	t + 3
ME	16.8	16.2	15.6	14.9	10.1	9.5	8.8	8.1	7.2	6.0	4.7	3.1
ME (%)	68.8	66.6	64.1	61.1	41.6	39.0	36.2	33.1	29.3	24.8	19.2	12.6
RMSE	26.5	25.9	25.4	24.7	20.8	20.2	19.6	18.9	18.5	17.1	15.5	13.8
RMSE (%)	108.5	106.3	104.0	101.4	85.5	82.9	80.2	77.5	76.0	70.1	63.5	56.8
EF	−0.1	−0.1	0.0	0.0	0.3	0.3	0.4	0.4	0.4	0.5	0.6	0.7

July–August due to adaptation or growth, or alleviation of inhibitory effects, then this could have caused the rapid increase in CH_4 emissions observed, which the two empirical models were both unable to reproduce accurately, neither with the default parameterisation nor by manipulation of storage temperature or parameter settings (Fig. 2).

If indeed there are seasonal dynamics in methanogenic potential resulting from adaption or growth, and seasonal variation in management routines for feeding fresh manure to the storage, then submodels with individual parameterisation of ln(*A*) for each time period and management practice may be better able to describe patterns of CH_4 emission during extended storage. Management practices such as cleaning between collection periods, or acidification, can also lead to process instability (Massé et al., 2008; Petersen et al., 2016b) that would require a customised parameterisation. Petersen et al. (2016a) described an in-vitro assay and algorithms to estimate ln(*A*) in slurry samples based on CH_4 production rates at the ambient temperature. If further developed and validated, such an approach could be used to analyse manure samples and parameterise a model representing individual storage units and periods during the year, circumventing the need for assumptions regarding methanogenic potential.

5. Conclusions

The present study indicated that more than two thirds of GHG emissions from untreated manure and digestates were accounted for by CH_4 emissions, with only minor contributions from N_2O and NH_3. The hypothesis that CH_4 emissions could be predicted by empirical models based on VS composition and temperature alone was not confirmed, since temporal dynamics of CH_4 emissions during a warm period in summer were not accurately reproduced. The hypothesis that AD treatment would reduce CH_4 emissions during storage compared to untreated slurry was confirmed. The AD treatment improved the overall GHG balance, although the gain was marginal where digestate was combined with untreated manure. We conclude that efforts to reduce GHG emissions from manure management chains must focus on mitigating CH_4 emissions during manure storage, with AD before storage as a potent option. A better prediction of the temporal dynamics of methanogenic potentials will be important to improve GHG balance calculations and inventories, and model simulations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.agsy.2018.07.009.

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